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SIGNIFICANCE OF HYDROGEN-ION CONCENTRATION IN DRINKING WATER AND PARTICULARLY FOR THE BUSINESS OF WATER SUPPLY[1]

By A. Massink[2] and J. A. Heymann[3]

PART I. GENERAL REVIEW OF HYDROGEN-ION SIGNIFICANCE WITH SOME DATA FROM OUR WATER SUPPLIES (MASSINK)

As several observers have already pointed out, Tillmans, by his introduction of the concept "aggressive CO_2," has had the chief share in bringing order and insight into this subject. In his book "The Chemical Examination of Water and Sewage" (1915) he has explained this clearly. He has recently, while this report was in the press, given an extension in which he has especially considered the hydrogen-ion concentration of water, a logical sequence of his earlier work. He emphasizes the significance of hydrogen-ion concentration for practical purposes.

It may be stated at once that for corrosive action of a water-supply the hydrogen-ion concentration is not the only factor—the oxygen, amongst others, plays a part. Tillmans' writings on aggressive CO_2 refer particularly to the reaction with $CaCO_3$ which proceeds as follows:

$$CO_2 + H_2O + CaCO_3 \rightarrow Ca\,(HCO_3)_2$$

until equilibrium is attained.

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[1] This paper was sent to Abel Wolman by Dr. Massink after he had read the former's paper on "Coöperative Research in Water Purification" presented at the Montreal Convention. The paper is in two parts, the first by Dr. Massink and the second by Dr. Heymann. Both were written in Dutch and were translated into English by Frank Hannan, chemist of the Toronto Water filtration works; the translation was prepared for publication by Mr. Wolman. Discussion of this paper is desired and should be sent to the Editor. The Publication Committee feels that important papers on water supply, even though highly technical, should appear in the Journal, as the chief American repository of valuable information on water supply in all its aspects.

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If the CO_2 content of the water is below the equilibrium value, then the reaction goes in the other direction:

$$Ca\ (HCO_3)_2 \rightarrow CaCO_3 + H_2O + CO_2$$

also to attainment of the equilibrium.

With respect therefore to the "aggressive CO_2" there are three cases possible: 1, The CO_2 concentration may be exactly that which equilibrium demands. 2, The CO_2 concentration may be greater (aggressive). 3, The CO_2 concentration may be less (reverse of aggressive).

In water supply, we are principally concerned with corrosive action on metals, in which the oxygen also plays a considerable part, inasmuch as when both a high oxygen concentration and aggressive CO_2 are present together, we may expect more corrosion than from aggressive CO_2 only. When we estimate for a given water the aggressive CO_2 according to Tillmans, we are estimating the CO_2 which acts on $CaCO_3$; for other materials other considerations must be taken in account.

It also is clear from the basic notion of aggressive CO_2 that it is not the hydrogen-ion concentration alone, but this taken in conjunction with the other constituents, which is of significance. One cannot, for example, say that a water with a hydrogen-ion concentration below this or that value is "aggressive" and above it, "not aggressive." For instance it might be imagined that pH = 7, corresponding to exact neutrality would be such a limit. But this is not so. The free CO_2 and HCO_3^- ion concentration must both be taken into account. Indeed, it is a well-known rule that a soft water becomes aggressive more readily than a hard.

HCO_3^-	FREE CO_2	HYDROGEN-ION CONCENTRATION	HCO_3^-	FREE CO_2	HYDROGEN-ION CONCENTRATION
mgm.	*mgm.*		*mgm.*	*mgm.*	
14–111	0–1.75	8.3–8.1	263.0	20.75	7.48
125.0	2.4	8.1	277.0	25.0	7.43
139.0	3.0	8.05	291.0	29.5	7.38
152.0	3.9	7.96	305.0	36.0	7.31
166.0	4.8	7.92	319.0	40.75	7.28
180.0	6.0	7.85	333.0	47.0	7.23
194.0	7.5	7.8	347.0	54.0	7.19
208.0	9.25	7.75	360.0	61.0	7.16
222.0	11.5	7.66	374.0	68.5	7.13
236.0	14.1	7.6	388.0	76.4	7.09
249.5	17.2	7.54	402.0	85.0	7.04

In Tillman's new publication above referred to, he gives free CO_2 and HCO_3^- concentrations which are in equilibrium with one another and the corresponding hydrogen-ion values. See table on page 240.

We do not need to follow this table further because, in drinking water at least, values for free CO_2 never reach even as high as those we have given.

An example will best serve to illustrate the use of these figures—Say a certain sample of drinking water is found to contain 300 mgm. HCO_3^- and 10 mgm. free CO_2, both very normal values. Seeing that 34 mgm. (more or less) of free CO_2 may occur in with 300 mgm, HCO_3^-, according to the table, before there can be any question of aggressive CO_2, this water cannot be aggressive, and the hydrogen-ion value must be greater than 7.34 which would be the table value for equilibrium. The calculation, in fact, following the well known formula:

$$[H^+] = K. \frac{[CO_2^-]}{[HCO_3^-]} \text{ and taking K. } = 3.04 \times 10^{-7} \text{ gives:}$$

$$[H^+] = 3.04 \times 10^{-7} \times \frac{2.27 \times 10^{-4}}{4.92 \times 10^{-3}} = 1.4 \times 10^{-8} = 10^{-7.85} \therefore \text{pH} = 7.85.$$

One may also proceed in another manner. Let the hydrogen-ion value be determined by one of the methods herein after given, or approximately estimated, and the HCO_3^- (or the free CO_2^-) content also determined; then one can see from the table whether the hydrogen-ion concentration corresponding to the value found for the HCO_3^- (or the free CO_2) is lower (aggressive) or higher (not aggressive).

The latter seems to me in general preferable for a HCO_3^- determination (titration with $\frac{N}{10}$ acid in presence of methyl orange) is simple to effect (much more practical than the apparently equally simple but in fact demanding much experience CO_2 determination) and a tolerably exact colorimetric hydrogen-ion estimation can easily be made. Fairly accurate conclusions as to presence or absence of aggressivity can be drawn.

From the table as given the following conclusions can also be drawn:

The table is continued almost to a hydrogen-ion value of 7. This corresponds to a bicarbonate hardness of $\frac{402}{61} \times 2.8$ — 18.5° (German degrees of hardness) on the understanding that there is no question of water containing alkali bicarbonate. As a rule the temporary hardness of tap water is considerably lower. Thus if a tap-water has a hydrogen-ion value of 7, it is almost certainly aggressive. Colorimetrically we may express this as follows: such water will react acid or at least very near the acid limit, with neutral red. The range of this indicator runs from pH = 6.8 (acid) to pH = 8 (alkaline). An acid reaction toward neutral red is thus an indication that the water is almost certainly aggressive. The matter of aggressivity, however, depends on the composition. Thus a very soft water (moor-water) with a low HCO_3^- content will be much more aggressive than a water with a temporary hardness of 10° (218 mgm. HCO_3).

One cannot, however, reverse this rule: A neutral reaction toward neutral red (about pH = 7.5) can very well be exhibited by an aggressive water: as one can readily see from the above.

From the examples given it should be clear, as we have already stated, that for the hydrogen-ion concentration of a water the free CO_2 and the HCO_3-ion play an important part. Just as in physiological fluids the hydrogen-ion concentration is regulated by the so-called "buffer" substances, these are also supplied by nature in water, and chiefly in the form of the bicarbonates. The poorer, then, a water is in these (moor-waters), the more readily is the hydrogen-ion concentration affected by varying influences (chiefly in this case CO_2); the water can thus become aggressive. Of this we shall see examples later in the data of our water supplies.

Naturally there is a very intimate connection between the composition (especially buffer-content, pH, etc.) of the soil and of the water that is, or has been, directly in contact with it.

Before leaving Tillman's table we should also mention the following:

In an article "On the connection between certain concentrations in the equilibrium between aqueous carbonic acid and $CaCO_3$," two curves (A) and (B) are traced for the relation of $[H^+]$ to $[HCO_3^-]$:

$$\text{(A)} \quad [H^+] = 2.29 \times 10^{-8} [HCO_3^-]^2$$
$$\text{(B)} \quad [H^+] = 2.07 \times 10^{-8} [HCO_3^-]^2$$

For brevity, refer to the article in question for the deduction of the curves. The table, already given, is graphically presented in figure 1. The continuous line shows the values deduced according to equation (A). The broken line represents Tillmans' table, and differs but slightly from the values obtained by Auerbach's equation (B), which would run parallel to the continuous curve given and slightly above it.

Just as one has, following Tillmans, a criterion with respect to aggressive CO_2 by comparison of the actual concentration of free CO_2 with that concentration given by him as corresponding to the known HCO_3^- concentration, so one can also from the figure form an opinion of the aggressivity of the water, when one knows the pH and the HCO_3^- concentration. If with a given HCO_3^- content the pH is lower than that given by the continuous curve (theoretical curve) or the broken curve (Tillmans' empirical curve), then that water will be aggressive; if higher, not aggressive. Consequently in the first case marble will be dissolved; in the second $CaCO_3$ will be deposited.

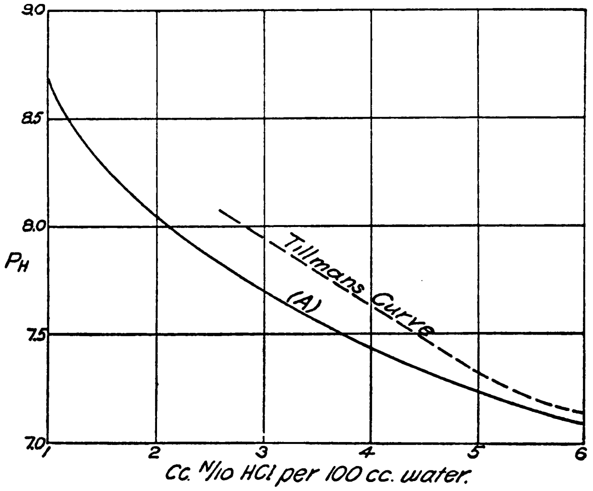

FIG. 1

We shall adopt for this purpose the empirical curve of Tillmans; but it must not be lost sight of that this curve, which represents the results of his experiments with $CaCO_3$, CO_2, and H_2O, cannot at the same time hold good with absolute exactness for all kinds of tap waters. In a certain sense it is also more prudent to take his curve than the theoretical, as it will decide for aggressivity rather earlier.

Before proceeding to the discussion of the data which the yearly examination of our water-supplies has furnished, a point deserving of closer consideration is: in what respect do the various properties of drinking-water depend on the pH?

Especially is an aggressive character imparted to the water by too high pH. Different phenomena may result herefrom.

1. The water-mains and other objects may be attacked. If this occurs with lead pipes, a lead-content dangerous to health may ensue; this case is thus chiefly of hygienic importance. We cannot further consider it here, because it needs an extensive independent research.

In case of pipes of other material the matter is rather of technical importance. One important consequence may be the so-called "re-ironing" by which the results of iron removal are to a certain extent rendered nugatory. The aggressive CO_2 first forms $Fe(HCO_3)_2$ (ferrous bicarbonate), which can remain in solution so long as the oxygen present is insufficient for completion of the following reaction:

$$4\,Fe\,(HCO_3)_2 + O_2 + 2H_2O = 4\,Fe\,(OH)_3 + 8\,CO_2$$

The CO_2 is thus reproduced. This last reaction is the regular iron-removal reaction which naturally takes place in the iron-removal installation, and *not* in the mains.

A case of this "re-ironing" came under my notice in a private water-supply in S. Limburg. The water contained about 40 mgm. CO_2 and about 25 mgm. HCO_3^- and was "de-ironed" in a closed apparatus. After the "de-ironing" the water carried about equal quantities of CO_2 and HCO_3^- and gave rise to iron solution from the mains. Acid neutralization was here the remedy indicated.

Sometimes cases occur in which the water becomes more acid on boiling, as appears occasionally to be the case with water from the Uden reservoir. Such water is of course absolutely unsuitable for any kind of industrial use, notwithstanding its softness, which in water otherwise suitable is a desirable quality in boiler-feed water. This phenomenon does not seem to have cropped up in any of our public supplies. On the contrary in the vast majority of cases the water becomes alkaline to phenolphthalein on boiling, so that this may be said to be a favorable showing as judged by this "boiling test." If we agree to call this result by the boiling test "negative," then a positive result (e. g., Uden) is to be regarded as unfavorable. The cause for this acidification on boiling cannot yet be satisfactorily explained. Probably after some time it will be cleared up from analytical data.

2. Greater difficulty in iron-removal. The Limburg water above mentioned was very difficult to de-iron, especially in a closed apparatus.

The water of the Coevorden supply, which shows considerable similarity to the above, gives rise to the same difficulties. The raw water will remain absolutely clear for days, even when left in a bottle in contact with air, and only slowly develops turbidity. Probably the very high SO_4^{--} concentration plays a considerable part in this. One is dealing, as a matter of fact, with a solution which approximates closely to a dilute $FeSO_4$ solution and is more stable than a $Fe(HCO_3)_2$ solution.

A high concentration of Cl^- or SO_4^{--} together with a low concentration of HCO_3^- has thus an unfavorable influence on the iron removal, which is still more pronounced when CO_2 is also present.

Occurrences of artesian water have come under the author's notice which are not suitable for drinking, which showed at first an alkaline reaction to methyl orange but contained large quantities of CO_2, Cl^- and SO_4^{--} and much ferrous iron in solution and which, by degrees, showed a steadily increasing acidity toward methyl orange, due to formation of basic ferric compound (chloride and sulphate and free mineral acid.) The disappearance of Fe^{++} and the increase in Fe^{+++} could be simultaneously observed.

This case is, of course, a very extreme one such as one cannot often meet in drinking water; the S. Limburg and Coevorden waters are weak analogies.

Already in 1911 Baskerville and Stevenson showed that Fe in acid and neutral solution at room temperatures is very slowly oxidized in the absence of catalyst (platinised asbestos), but rapidly, on the contrary, in alkaline solution. (Jour. Amer. Soc. Chem., 1911, 1104.)

Hence it is that soft iron waters with relatively high CO_2 content are difficult to free from iron.

3. The significance of hydrogen-ion concentration in drinking water seems also to extend to a department which is of less concern to the chemist than to the physician, namely mineral waters.

4. Also in the chemical analysis of water there are instances of the hydrogen ion concentration being of significance. Thus, for example, in the decolorization of deep brown humus containing waters ("veenstreken") previous to analysis, by means of a suspension of Fe $(OH)_3$, the decolorizing action of which increases when the HCO_3 content of the water has been reduced by addition of acid.

Further the precipitation of silicic acid from drinking water by means of soda and alum, where the reaction toward phenolphthalein is of importance. These examples have not yet been treated of in close connection with the pH, but all probably depend on this connection.

Data respecting the hydrogen-ion concentration of our water supplies

The yearly examination of the water of the Netherland water-supplies by the Central Laboratory has yielded considerable material for the preparation of this report. In 1919 all the pumping stations were visited and determinations of free CO_2 and HCO_3^- (amongst others) carried out on the spot; further the hydrogen-ion concentration was colorimetrically estimated, in which also the freshly pumped raw water was compared with the filtered water before it was "purified" by one or the other process. Also the Heyer marble test was made on the spot on the filtered water. As soon as possible after arrival at the Central Laboratory the hydrogen-ion concentration of the raw and filtered water was determined. During 1919 this was done by the well known Sörensen colorimetric method. Naturally there are certain disadvantages inseparable from this way of working; for example the influence of the alkali of the glass became noticeable during the storage of the water in the bottles (3-litre, nearly or quite full), also Kahlbaum's primary and secondary phosphates were not to be obtained, so that these had to be made up from phosphoric acid solutions of titrated strength and NaOH solution. The solutions specified by Michaelis were employed. Neutral red and methyl red were chiefly used as indicators; alpha-naphthol phthalein to a less extent. This latter indicator was found to give in general too low a value for hydrogen-ion concentration, which is in agreement with Sörensen's results unless the "salt error" of the indicator is taken into account. As this indicator is suited for the range between neutral red and phenolphthalein (pH 8–8.3) the values in this range could not be determined with thorough exactness.

It is true that neutral red does not always give even approximate results. Thus, for example, it was remarked in the early part of 1920 that while two samples gave the same result electrometrically, the tints with neutral red differed—so that the water of greater salinity appeared more acid. This too is in line with Sörensen's experience. Thus one can only regard the colorimetric method as an approximate one, which may or may not be sufficiently accurate for practical work but does not give absolutely correct values, as indeed is generally known.

The electrometric method just mentioned is, on the other hand, more exact. In 1919 the necessary installation was not complete, so that only in 1920 could work be done with it. The installation used is almost identical with that described by Kolthoff but a calomel electrode with saturated KCl solution was used. The firm Marius sells a round "Schakeltafel" to which the galvanometer is fixed which greatly simplifies the setting up. In calculating the results, use is made of Sörensen's curves to which an "exponential line" for saturated KCl must be added. After taking a reading one has then the hydrogen-ion value required in less than a minute. It was observed that attainment of equilibrium of the hydrogen electrode was slower and the reading less sharp, according as the water is poorer in salinity ("mixture poor in buffer substances").

The phosphate solutions last used in 1919 were examined electrometrically as a control. Equal concentrations of primary and secondary phosphates gave hydrogen-ion concentrations as follows: electrometric, 6.85; Sörensen's figure, 6.81; thus they were in good agreement.

In 1920 as many as possible of the samples examined were tested electrometrically for hydrogen-ion determination, while in 1919, as explained, the colorimetric method was used.

In 1919, moreover, as already mentioned, the marble test was carried out. After the lapse of 3–4 days for very soft waters, and about a week for harder waters, the hydrogen-ion concentration value of the water from which the marble powder had settled out was again determined (colorimetrically; some also calculated from the values found for free CO_2 and HCO_3^-) and the value found compared with that of the filtered water. In this comparison, three cases were possible:

1. After the marble test, pH greater; aggressive water.
2. After the marble test, pH less; non-aggressive water.
3. After the marble test, pH unchanged.

This first case holds for water with aggressive CO_2: the aggressive CO_2 brings $CaCO_3$ into solution in the form of $Ca(HCO_3)_2$, so that, as compared with the filtered water, the CO_2 content is lower and the HCO_3^- content higher, whereby the hydrogen-ion concentration becomes greater.

The second case holds for non-aggressive water in which, accordingly, the free CO_2 content is not enough to retain the alkali-earth bicarbonates in solution. It is not to be imagined that this $CaCO_3$ precipitation occurs rapidly; this takes place very slowly except when a considerable deficiency of CO_2 is found combined with a very high HCO_3^- content (not usual in drinking water).

After the marble test the CO_2 content has become higher and the HCO_3^- content lower:

$$Ca\ (HCO_3)_2 = CaCO_3 + H_2O + CO_2,$$

whereby, therefore, hydrogen-ion concentration becomes lower. This is very frequently the case with drinking waters.

The third case holds for the waters in which there is equilibrium between the CO_2 and the HCO_3^-. Some drinking waters come under this category as being almost in this condition.

In the first case the equilibrium is more readily attained than in the second: this is because the solution of the marble takes place more rapidly than does the $CaCO_3$ precipitation.

The figures embodying the results of the examination of the water supply samples by the Central Laboratory are given in the following table.[4]

The results for the most part relate to the examinations in 1919. As the variations from year to year are not great it was preferred to give the CO_2, HCO_3^-, etc., values for the same year in which the colorimetric pH determinations and the marble tests were made. These results for HCO_3^- and CO_2 can also be obtained from the report which will probably soon be published for the "Vereeniging voor Waterleiding belangen." The electrometric pH determinations were made in 1920. Probably most water supplies show no considerable variation in the pH so that a comparison with 1919 is fairly permissible. The figures for HCO_3 and CO_2, for example, over the various years vary but slightly. Naturally the time which elapses from the taking of the sample is of influence, by which here and there variations of some account appear. As the colorimetric determinations are more numerous than the electrometric, the conclusions, positive or negative as to aggressiveness, were drawn from the former.

The following supplies have certainly aggressive CO_2 (that is both colorimetrically by the marble test, and according to Tillmans' curve):

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[4] The tables accompanying Dr. Massink's article were not submitted by Mr. Wolman, as they were numerous and not needed for clarity.

Almelo, Amsterdam (Westwevold), etc., 31 all told; that is about 30 per cent of our supplies.

By far the greater number of these belong to the moor-waters which give a supply with low bicarbonate hardness. There are two surface water supplies among them, Groningen (de Punt) and Leenwarden, in which by alum treatment the bicarbonate hardness is so reduced that aggressive CO_2 has developed.

Also at Hoorn the water has been made aggressive because by the treatment with lime and sulphuric acid the bicarbonate-hardness is considerably reduced. The H_2SO_4 treatment converts the $NaHCO_3$ into Na_2SO_4.

With certainty, a very great certainty, the following are non-aggressive:—Alblasserdam, Alkinaae, etc., all told, 67, or about 65 per cent of our supplies, including among others, the river supplies (excepting Leewarden and Groningen, dePunt), and the dune supplies; in general those supplies with relatively high bicarbonate hardness.

In order to compare the results given by the chemical examination in the Central Laboratory with the results obtained in practice, which could therefore be considered as known to the various water supply operators, a questionnaire was sent to these with the following questions: the resulting answers are given and discussed below:

Question A. Has the presence of aggressive CO_2 been noted in your supply, in the raw or in the filtered water? If so, is this a constant feature?

Question B. How does the aggressive CO_2 manifest itself? What objects are attacked and with what result?

Question C. Is the aggressive CO_2 so troublesome that measures to combat it have been designed or undertaken? If so, what are these measures?

Question D. What has been the result of these measures?

As a result of the questionnaire the following was obtained:

Of the 106 water-supplies, 40 have answered that no evidence of aggressive CO_2 has been observed; 11 have answered that it has been observed; 50 did not answer; a few answered very vaguely. Of the 50 not answering, 22 should, in accordance with the examination which the author made, have had aggressivity to report.

Discussion of results of questionnaire. From the results the following can be inferred:

1. That from about half of the water supplies answers have been received.

2. Of those who have answered and in the sense that manifestations of aggressive CO_2 are positively reported, about 20 per cent report such manifestations.

3. Of those who have not answered, probably 45 per cent would have had such manifestations to report.

A selection from the data obtained from the operators is appended.

Amsterdam (Westerveld): Aggressive CO_2 present all the time. This appears from the analysis and the marble test. In practice this manifests itself by non-formation of a protective coating of $CaCO_3$, so that metals (iron, lead, zinc) are powerfully attacked. Amongst the measures taken against it is the use of tin-coated pipes to prevent lead being taken into solution. This object has been attained.

Apeldoorn: Manifestation of aggressive CO_2 can only be attributed to the organisms in the mains, which deposit as a very firmly adherent coat. Measures against it have not yet been needed or planned. Unfortunately some of the larger mains will have to be repaired.

Deventer: Aggressive CO_2 has been the chief cause of lead appearing in the water. After the inauguration of the closed iron-removal plant, this was the case. There is now an installation to remedy this defect.

Enschede: Aggressive CO_2 is all the time present in the raw water. Pipes of lead or of unprotected iron are of no use. The lead-solvent power of the water is so great that only tin-lined lead pipes can be employed. The aggressive power is greatly reduced by spraying ("rieselen") and the lead solvent action is nearly altogether removed; each case reduced to one-tenth.

Gouda: The raw water (river water, from time to time mixed with pond water) does not attack the iron of the pipes. The filtered water was formerly treated with alum resulting in the pipes being attacked with formation of bumps ("red water"). After the abandonment of the alum treatment these phenomena have disappeared, probably permanently. To remove the aggressive CO_2 a layer of 15 cm. "schelpen" was spread on the slow sand filters, which caused a considerable increase in the filter pressure and had to be rejected.

Den Helder: From some iron being attacked it can be concluded that corrosion is in evidence, but only in the raw water. These manifestations do not occur in the centrifugals nor in the drawn iron mains; they are found on forged-iron articles (stays and bolts of filters). As they do not amount to very much, no measures have been needed to combat them.

Helmond: Rust formation was occasionally noted in the cast-iron mains, which was ascribed to free CO_2. No measures necessary.

Maastricht: The blades of the high-pressure centrifugal pumps, both of bronze and of iron, are very rapidly corroded by the water on the suction side. This was set down to aggressive CO_2. As means to combat it, there have been recommended, first, powerful exhaustion of the air or vacuum liberated gases by a vacuum pump before the water enters the centrifugal; second, tinning the vanes and guides. As yet we have no experience of result.

Venlo: Aggressive CO_2 observed all the time. This causes corrosion in the main, by which, during heavy demand, brown coloration of the water; water-meter parts attacked. By vigorously scouring the mains the brown-water troubles have been successfully combated. Neutralization of the acid is under consideration.

Wageningen: Aggressive CO_2 observed all the time. After some years' use some of the wells sanded up and it appeared that the brass filters were entirely corroded through solution of the zinc. After this filters of red copper were used which have remained intact. Cast-iron pipes were attacked and lumpy deposits appeared owing to which mains of small diameter no longer carried sufficient water. Cast asphalted steam pipes both in service mains and in houses choked up and rusted through. Repairing the mains destroyed the asphalting whereby the rust formation became more intense. In 1915 a trial plant for vacuum de-acidification (Sürth, Köln) was set up with favorable results. Too high a price unfortunately prevented its definite adoption. Consultations with Dr. Meerburg took place with reference to lime addition for acid removal. Most of the rust formation seemed to occur in that part of the system where most water was flowing and not in the dead ends. No organisms were found in the pressure mains ("fersleidingen").

Zwolle: It has been several times found that the waterpipes through the whole thickness of metal from inside to out had been changed into a carbon-like mass. This also occurred in the return circuit ("retourklep") of the high pressure apparatus. This may have been caused by aggressive CO_2. (This phenomenon is known as "verpotlooving.")

Comparing the water-supplies which, as seen from their answers to the questionnaire, show signs of "aggressiveness," with those for which this should be the case according to the examination by the Central Laboratory, the following appears:

In the following instances, signs of aggressivity, although they have no aggressive CO_2: Deventer, Gouda, den Helder, Maastricht. But the first two no longer show it. Other factors must therefore come into play here besides the free CO_2; among which oxygen should certainly be noted as taking the most prominent place. Both de-acidification and deaeration should bring about an improvement. Deventer chose the former plan and Maastricht advises the latter.

From the answers received, few in number though they be, of the water-supplies that have aggressive CO_2, it is yet clear enough how important the matter is for the water-supply-business. On the varying local factors it will depend whether deacidification is called for. When, for example, it is found too late that a water supply has aggressive CO_2 and the material for the mains has not been so selected that undesirable results are avoided, then deacidification will be necessary. Also the choice of the de-ironing system is dependent on it. Thus, in cases where aggressive CO_2 is present (or, in general, much free CO_2) a closed system should not be used.

Conclusions. 1. From the literature and from practice it appears that hydrogen-ion concentration is of significance for drinking water and the water supply business.

2. From laboratory examinations and local observations, some 30 per cent of our (Dutch) water supplies give aggressive water, inclusive of the moor-water supplies and a few that use alum and such like.

3. In the questionnaire on aggressive CO_2, about half the water supplies have sent in replies; of these 20 per cent report signs of "aggressiveness," with important data. These signs are to be ascribed in part to the hydrogen-ion concentration and in part to other causes.

PART II. THE SIGNIFICANCE OF pH FOR DRINKING WATER, IN A PARTICULAR WATER SUPPLY IN ITS SUCCESSIVE PHASES (HEYMANN)

In the compilation of a report on the above, it seemed more practical to divide the task between Dr. Massink and the author in this way, that he devoted himself rather to the significance of pH for drinking water generally, while the author paid attention to its particular significance for the water supply business. In this the author has kept in view particularly the Amsterdam water supply. Seeing that this is composed of three separate supplies with relatively widely varied composition, it is fair to attribute a general significance to the report.

While Dr. Massink devotes his attention to drinking water supplies, the author has here equally considered the Amsterdam Vecht-water supply which is chiefly for industrial purposes. None the less, the purification of this supply is effected with so much care that the effluent could very well compete with many a Dutch drinking water.

In an article published in the *Chemical Weekblad*, 1919, pages 105–120, the author has already described this Amsterdam supply business in its chief outlines, and in order to avoid too much useless repetition, he will refer now and again to that article for fuller details.

The three Amsterdam supplies are the Dune water, the Bron water and the Vecht water.

The collection area of the dune water extends over nearly the whole of the dune district from Zandvoort to Noordwijk. The water drawn from this district is entirely derived from the rainfall, for various researches have shown that there can be no question of an underground flow hitherward from the East. Although in the final analysis, all our drinking water is, as a general rule, derived from the rainfall, it is not usually practicable to follow the water in its course from the moment that, in the form of rain, it strikes the earth to the moment that it leaves the tap. For the dune water this is, however, the case: by which statement we do not mean that absolutely every change the water undergoes is fully explained.

Dr. vander Sleen gives in his dissertation an exhaustive treatment of the chemical activity of the dune water at different depths and tries at the same time to account for the changes in chemical composition which take place in the earth beneath our dunes; in which he has given the importance they deserve to the carbonic acid and carbonates, which, as we shall see, determine completely the pH of the dune water. Of aggressive CO_2 there is no mention in this dissertation, while the pH question is also not raised, which last can hardly cause any surprise seeing that the study of it was still in the first stage of its development, especially in connection with its practical applications.

Before giving any figures the author acknowledges that he has only engaged in the study of pH for a relatively short time, so that probably the values here given will later, as a result of further research, be considerably changed. This applies more especially to the surface waters, the pH of which stands in the closest kind of relationship with the algae living in it, and in which a combination of circumstances may bring about wide changes from the average.

As the CO_2 content of rain water in the winter months just passed, values from 1.4 to 4.2 mgm. per litre were found, while the temporary hardness (0.70 to 0.90) was so small that, following Tillmans' tables, we can regard the CO_2 as practically entirely aggressive. The pH varied from 6.90 to 7.25.

As soon as this water reaches the earth important changes in its composition occur. If the earth is covered with vegetation and greater or less layer of humus, then the CO_2 content must increase considerably, especially in places where decaying vegetable matter furnishes a favorable culture medium for the bacteria and gives rise to free disengagements of CO_2. If the soil is bare and has little organic matter, as is the case over large areas in the dune district, then the CO_2 increase from the influence of the earth is small. Directly coupled with this phenomenon is a reduction of the free CO_2 in this way that a portion of it unites with the almost universally present $CaCO_3$ which thus goes into solution as $Ca(HCO_3)_2$. The $CaCO_3$ content of our dunes varies between very wide limits; the old inland dunes are poor in lime, while the younger dunes, which comprise the greater part of the dune district of the Amsterdam water supply, are very rich therein.

The amount of vegetation and the thickness of the humus layer on the one hand and the lime content on the other, thus constitute the factors which in the main determine the CO_2 content of the water percolating into the earth. As both these factors may vary widely, it is not surprising that in the upper layers of the ground water we find widely varying composition of the water as the figures in table 1 show.

TABLE 1

WATER LINE	KIND OF GROUND	pH	$\frac{(H)}{10^{-7}}$	CARBONATE HARDNESS IN DEGREE	FREE CO_2	AGGRESSIVE CO_2
Zwarteveld no. 5..	Tilled, thick humus layer	7.35	0.45	19.3	49.0	−47.7
Westerveld no. 6..	Light growth	7.51	0.32	10.4	17.4	3.4
Westerkan W. no. 4	No growth	7.70	0.20	11.2	11.5	−4.5
Westerkan W. no. 7	Very light growth	7.75	0.18	8.7	9.0	0.8
Vinkenveld F.....	Tilled, practically no humus	7.75	0.18	7.0	7.1	3.2

Notwithstanding the high content of free CO_2 met with in the first sample beneath tilled land, no aggressive CO_2 appears to be present on account of the high carbonate hardness, a consequence of the lime-richness of the soil. The last sample exhibits the very opposite; little free CO_2 but at same time small carbonate hardness and consequently relatively high aggressive CO_2. Just as do the figures for total carbonic acid content, so too, only more so, the pH value gives quite a false picture of the aggressivity of the water.

A part of the dune water is derived from the upper levels along the coast line, the so-called "upper water," while another part, the deep dune water, is drawn from a formation at a depth of between 25 and 45 meters by tube wells, the so-called "Eemstelstel." Both kinds are collected in shallow canals which intersect the dune district. From a number of the tube wells, just as for the previously recorded samples from the upper layers, determinations were made of the pH, the carbonate hardness and the free CO_2: and from the last two the aggressive CO_2 calculated. Some of the results are given in table 2.

TABLE 2

STATION	pH	$\frac{(H)}{10^{-7}}$	CARBONATE HARDNESS IN DEGREE	FREE CO_2	AGGRESSIVE CO_2
Van Stirumkanaal					
50	7.47	0.34	15.0	29.1	−15.1
55	7.44	0.37	15.0	31.8	−13.4
60	7.37	0.43	14.3	31.8	−5.7
65	7.48	0.33	11.8	23.3	2.4
70	7.49	0.33	10.4	17.9	3.7
75	7.53	0.30	12.5	21.2	−2.2
80	7.53	0.30	10.9	19.1	2.6
Westerkanaal					
10	7.47	0.34	15.7	30.0	−21.6
15	7.49	0.33	14.0	22.3	−12.7
20	7.62	0.24	15.7	19.3	−32.1
25	7.49	0.33	14.8	24.9	−17.5
30	7.50	0.32	13.4	2.23	−7.4
Boogkanaal					
5	7.67	0.21	13.0	15.7	−11.5
10	7.65	0.22	14.1	17.6	−18.3
15	7.65	0.22	14.1	17.6	−18.3
45	7.68	0.21	14.1	18.0	−17.9
50	7.78	0.17	13.2	13.1	−15.4

For the water of the wells of the Van Stirum and the Wester Canals, which for almost their entire length run parallel with the sea coast, the pH varies but little. Carbonate hardness and free CO_2, on the contrary, show relatively wide variations. But the aggressive CO_2 gives here very remarkable figures or rather the deficiency of CO_2 from the quantity which should be present for equilibrium with the $Ca(HCO_3)_2$ content, which for shortness is called the "appropriate" (bijbehoorend) CO_2. Some of the Van Stirum Canal wells give aggressive water: the greater part of the wells of this canal and all those of the Wester and Boog canals show a greater or less deficiency of "appropriate" CO_2. Very probably there was originally an equilibrium; that is' to say, the water which penetrated the earth continued to take up $CaCO_3$ until all the aggressive CO_2 had disappeared and the CO_2 remaining free was just in equilibrium with the $CaCO_3$ content which the water then had.

The composition of the dune water is not readily determined, inasmuch as the water is not collected as such and this is for some time enclosed in the canals; consequently such changes take place, reflected again in the pH, that analysis can no longer give a just picture of the true composition of this water.

The pH of all the water which is of any importance in the Amsterdam supplies is regulated by the presence of CO_2 and carbonates. It is true there is in the dune region a well district which gives water with humus acids: but these wells which give an inferior water are in ordinary times not drawn on and need an apparatus for direct pH determination, so it has been impossible to extend the experiments to them.

TABLE 3

KANAAL	pH	$\frac{(H)}{10^{-7}}$	CARBONATE HARDNESS IN DEGREE	FREE CO_2	AGGRESSIVE CO_2
v. Stirumkanaal	8.10	0.08	13.0	4.9	−22.1
Nieuwe kanaal	8.05	0.09	13.8	6.0	−27.3
Zwarteveldkan	8.10	0.08	12.2	4.6	−16.8
Boogkanaal	7.85	0.14	14.3	10.2	−27.5

In the shallow open canals through which the water slowly flows, it loses first a share of its CO_2 to the air, while a considerable proportion is assimilated by the numerous algae growing in these canals. If the well water contains any considerable concentration of iron, then, for two reasons, we may expect a lower pH in the canal than for a water less rich in iron, of otherwise identical composition. First, free CO_2 is liberated by decomposition of $Fe(HCO_3)_2$; and, in the second place, the ferric hydroxide formed hinders by light absorption the algae growth. This phenomenon is especially noticeable for the water of the Boog canal, as the figures in table 3 show, which refer to samples drawn from the delivery end of the canals.

These determinations were made in February; in spring and summer still lower pH values are to be expected.

The canal waters are collected in the Oranjekom, a reservoir about 1.5 meters deep with an area of about 2 hectares excavated on the dunes. Form this it is conveyed by a main 1360 meters long to a pair of raw water reservoirs. For want of light the CO_2 assimilation process is at a standstill in the main and in these reservoirs, while the organisms of those kinds which are in the water by their respired CO_2 bring down the pH value somewhat.

From these raw water reservoirs the water is pumped on the pre-filters, pits of 100 square meters area, in which there is a meter-thick layer of gravel ("grint") of 2–6 mm. size. These pre-filters are set up in a shed ("loods)" where the light is mostly cut off, so that no algae growth takes place in the upper water. By the very great number of bacteria that flourishes in these filters, a very considerable portion of the soluble organic matter of the water is oxidized, while otherwise no chemical changes occur which influence the pH. But the fact just mentioned is the cause of a relatively great reduction in the pH.

The water thus prefiltered and now perfectly clear comes on to the after filters, basins of an average area of 3000 square meters which have a layer of dune sand about 100 cm. deep. In the upper water of these filters a very luxuriant growth of algae takes place. In the winter and early spring the diatoms predominate while in the rest of the year the filament forms have the upper hand. In this connection, the diatoms effect a very marked assimilation of CO_2. Tillmans says in an article which is discussed a little later that those cases in which, along with much HCO_3 there is but little free CO_2, in actual practice play an important part, because there must always be free CO_2 present with $Ca(HCO_3)_2$ if the latter is to be stable. He goes on to specify strong aeration as the process by which the CO_2 content of the water can be brought down to a very small amount. He very improperly here leaves altogether out of consideration the algae: and they, indeed, constitute a very powerful means of removing CO_2 from the water. While by spraying the water as is done at Leiduin in the prefilters, one can reduce the CO_2 concentration by a few milligrams in the upper water of the after filters, in sunny weather the CO_2 concentration goes down to nil. Up to now the author has never observed complete absence of CO_2. One proof of this disappearance of CO_2 being due in practice to biological action is that the assimilation process is at a standstill during the night.

One often sees the opinion advanced that a deficiency of "appropriate" free CO_2 gives rise to an immediate deposition of $CaCO_3$. Nothing is less true. The dune water carries on an average 385 mgm. $Ca(HCO_3)_2$ per liter. When from this water all the free CO_2 is removed, as may occur in the upper water of the filters in the manner just described by means of the algae, nevertheless this water remains perfectly clear for days. One may even drive off the CO_2 by boiling without bringing about separation of $CaCO_3$. The pH of such water is 8.25 to 8.30, corresponding to a hydrogen-ion concentration of 0.056 to 0.050.

In the passage through the sand bed of the after filters some of the organic matter in solution is oxidized by the bacteria, whereby the CO_2 concentration and with it, of course, the (H^+) increases. Nevertheless this last is always lower than in the "fore-filtrate," owing to the strong reduction it suffers before the water percolates into the sand bed.

The filtered water is collected in a purified water reservoir and pumped from there by two mains to Amsterdam where it again flows into a storage reservoir before finally being brought into the city system. During the whole journey from the filters to the city mains, the water undergoes almost no alteration; neither the CO_2 content nor the pH is altered. Here especially is it most clearly manifested that a deficiency of "appropriate CO_2" does not give rise to a rapid separation of $CaCO_3$, even when the water is in contact with $CaCO_3$ crystals. The deficiency of "appropriate CO_2" in the filtered water is always from 10 to 20 mgm. on an average. It is true that $CaCO_3$ is deposited in the reservoir, but the quantity is very small—the amount at Leiduin in the course of a whole year is only a few dozens of kilograms. The $CaCO_3$ which separates in the mains partly attaches itself to the walls and thus forms the protective layer: while that part which separates free in the water is carried forward by the stream and in the filtered water reservoir in Amsterdam it settles out. The amount of this last likewise only comes to a few dozens of kilogrammes in the year. While if all the calcium bicarbonate which is in the water in excess, in respect to the content of free CO_2, were to be precipitated as $CaCO_3$, and assuming the deficiency of "appropriate CO_2" at only 10 mgm. per liter, a matter of about 190,000 kgm. a year of $CaCO_3$ would accumulate in the filtered water reservoir.

The Vecht water supply formerly, as the name implies, drew its water from the river, the Vecht. At the beginning of the working, an arrangement was made by which water could also be taken from the Merwede Canal; and as this last appeared to be in some respects preferable to the Vecht water, mostly Merwede Canal water was used afterward. This water shows a considerably different composition from the dune water. It has a lower carbonate hardness and thereby more readily acquires aggressive CO_2. At the Weesperkarspel pumping station it undergoes a somewhat different treatment from that applied at Leiduin to the dune water. After flowing through a 4000 meter long main, it is pumped out of a relatively small raw water reservoir into two settling basins of 40,000 cubic meters content each, in order to settle out the larger impurities. The water is generally turbid and has a permanganate consumption of 15 to 40 mgm. $KMnO_4$ per liter. It has dozens of bacteria to the cubic centimeter and only a few algae. In short, CO_2 development is readily brought about in various ways and CO_2 absorption is hindered. In the autumn and winter when the algae life is reduced to a minimum and CO_2 assimilation is nearly at a standstill, a low pH value is found and the water shows aggressive properties. When on the other hand in the spring the algae and especially the diatoms come to the front the pH goes up and instead of an excess, there is a deficiency of "appropriate CO_2."

Until very lately the author had never noticed that the CO_2 in the sedimentation basins was altogether used up. This unusual phenomenon showed itself this year in March for the first time and lasted for some weeks. The water reacted more or less strongly alkaline to phenolphthalein. The pH ran from 8.3 to 8.7 with a HCO_3 concentration of 190 mgm. per liter on an average and a CO_3^{--} concentration of 0 to 6.6 mgm. per liter. The reason for the phenomenon seems to lie in the presence of a very great quantity of diatoms in the water. By count, for example, amongst others, 2,200 of these silicic algae to the cubic centimeter were found: and principally *Asterionella gracillima* and *Diatoma elongatum.* The water appeared slightly turbid from the diatoms and accompanying this phenomenon, as is no cause for surprise, was a supersaturation with oxygen.

From the sedimentation basins the water is led upon four filters, which are about one and one-half times as large as those of the dune supply, but in other respects, at least in all the chief points, constructed in the same way. The sedimentation makes the water less turbid; besides which it stands in the after filters only 75–100 cm. over the sand bed, so that the light has everywhere abundant access. As a result a luxuriant vegetation of algae is brought about, by which the same phenomenon may occur as was repeatedly observed at Leiduin, namely that on sunny days the CO_2 reaches almost total exhaustion. The pH reaches in this way values from 8.25 to 8.29. To total absence of free CO_2, that is, red coloration of water with phenolphthalein, it comes only in so far as experience to date can be taken as a guide, when the water carries a very great quantity of diatoms, as was the case in March and April of this year (1920).

The millions of diatoms which, specially in the spring, appear in the filters, are mostly benthonite forms which cover the sand bed as a more or less adherent layer. Massa's plankton forms, such as were found this year in the Merwede Canal, are exceptional, at least in the Amsterdam water supplies. Probably their appearance had some connection with the abnormally mild weather conditions of this spring.

The filter coat of the after filters completely retains the suspended matter, so that the water after passing through this stratum of algae is perfectly clear. However, it still has much organic matter in solution, which to some extent is attacked by the billions of bacteria inhabiting the sand bed, by which process CO_2 is developed. Thus the pH value is reduced during the passage through the sand bed. In the upper layers of the sand bed there is still for the most part a deficiency in "appropriate CO_2;" while, when leaving the filter, at least in the autumn and winter months, the water usually has aggressive CO_2. Besides being shown by the analysis, this can also be observed in practice from the fact that a little $CaCO_3$ can still be found in the filter sand, while in the filtered water reservoirs none is found.

The very rapid coming to life of the world of diatoms in March is the reason for the great alteration undergone by the pH value in this month, compared with the preceding winter months, during which the CO_2 development has the upper hand of the CO_2 assimilation.

The monthly averages given in table 4 bring out this clearly.

In consequence of the abnormally mild winter (1919–1920) we have just had, and in close relation therewith the relatively high temperature of the water, the algae growth was very strong even in

January, and consequently these figures are less striking than would have been the case under more normal conditions.

The Bron water supply is derived from the district all the way from Hilversum to Noorden. The water is drawn from the diluvial strata by 15 wells which have an average depth of 38 meters. This water is so pure and has so little iron that it can be carried into the transport main direct without any preliminary treatment. The composition of the water is practically constant.

The average carbonate hardness amounts to only 4.45°, so that here aggressive CO_2 may be expected much sooner than in the Merwede Canal water, although, then, the CO_2^- concentration is very low, viz., only about 6 mgm. per liter, yet fully 4 mgm. of it is aggressive, calculated according to Tillmans' tables.

TABLE 4

	SETTLED WATER				FILTERED WATER			
	pH	$\frac{(H)}{10^{-7}}$	Free CO_2	Aggressive CO_2	pH	$\frac{(H)}{10^{-7}}$	Free CO_2	Aggressive CO_2
January	8.0	0.10	4.0	−2.7	7.8	0.16	7.1	0.5
February	8.1	0.08	3.9	−6.4	7.9	0.13	5.7	−3.5
March	8.3	0.05	1.3	–	8.05	0.09	4.5	−4.2
April	8.6	0.025	0	–	7.9	0.13	4.9	−2.2

pH of 7.58 was found as the average for this water, corresponding to $(H^+) = 0.26 \times 10^{-7}$. Determination of the concentration of aggressive CO_2 according to Heyers' marble test gave results in good agreement with the calculated concentration according to Tillmans' tables.

In water which had 6.1 mgm. CO_2 per liter and 4.48 carbonate hardness consequently, according to Tillmans, with 4.4 mgm. aggressive CO_2, there was, after 4 days shaking with marble powder in a quite full stoppered bottle, a CO_2 concentration of 2 mgm. per liter; from which would follow an aggressive CO_2 concentration of 4.1 mgm. While the pH was originally 7.58, this rose by the marble treatment to 8.05 corresponding to $(H^+) = 0.09 \times 10^{-7}$. The new carbonate hardness was 5.05 from which taken in connection with the original carbonate hardness may be inferred that the water had 4.4 mgm. aggressive CO_2.

The aggressiveness of this water shows itself in practice by the fact that no protective coating of $CaCO_3$ is formed, consequently the metal of the mains is exposed to the corrosive action of the water.

The above mentioned determinations of the pH value were all carried out by the indicator method, using for the most part as standards KH_2PO_4 and Na_2HPO_4; while in the cases where pH was over 8.1, borax-HCl mixtures were mostly used. Neutral red was chiefly employed as indicator, which even for very small changes in pH gives considerable change in tint, and in this respect is far preferable to azolitmin, which was also sometimes made use of and which certainly has a wide range, but in which the color changes are much less striking. For water with pH over 8.3 phenolphthalein was used.

Not having an apparatus for direct pH determination, the work was exclusively colorimetrically, which was here always possible inasmuch as the author always had practically colorless water with which to work.

The indicator method in one respect is certainly preferable to the direct method. Quite apart from those cases in which the presence of ammonium sulphide renders the latter method unworkable, the determination can quite readily be made on the spot where the sample is taken. This is highly desirable whenever one has to do with water which has much CO_2, for notwithstanding every precaution, loss of CO_2 in transport can with difficulty be altogether avoided.

As to the manner in which the pH is expressed the method given by Tillmans is much to be recommended, namely in ten-thousandths milligrams H-ion per liter, which gives figures much more convenient for comparison than Sörensen's numbers. Hence it is that in the tables the author always gives the value of $\frac{(H^+)}{10^{-7}}$, corresponding to Tillmans' "h."

In the above referred to article of Tillmans, he gives formulae for the calculation of pH or h, from the content of free CO_2 and HCO_3 of the water, deduced from the mass action law of Guldberg and Waage. He differentiates four possibilities:

(a) Free CO_2 alone is present.
(b) Much free CO_2 and much HCO_3 are present.
(c) The water has much free CO_2 and very little HCO_3.
(d) The water has much HCO_3 and very little free CO_2.

The second case is the most usual in the business of water supply. From the equation $H_2CO_3 \rightleftarrows H^+ + HCO_3^-$ follows:

$$\frac{(H^+) \cdot (HCO_3^-)}{(H_2CO_3)} = K. : \text{or } (H^+) = K. \times \frac{(H_2CO_3)}{(HCO_3^-)}$$

As only a very small portion of the H_2CO_3 is ionised, we can replace in practice the (H_2CO_3) by the total concentration of free CO_2. Further, Tillmans assumes the bicarbonate to be almost completely ionized, so that we can assume for (HCO_3^-) the total concentration of HCO_3^-. Dividing the numerator and denominator of the fraction by *44,000* we get the concentration of the free CO_2 and the bicarbonate in milligram per liter, so that we can finally write the formula

$$(H^+) = K_1 \times \frac{\text{free } CO_2}{\text{bicarbonate } CO_2}$$

or, since $K_1 = 3.04 \times 10^{-7}$; approximately,

$$h^\circ = \frac{3 \text{ x free } CO_2}{\text{bicarbonate } CO_2}$$

Tillmans shows by calculations that we can in practice almost always make use of this simple formula. Only when the CO_2 concentration is very small in proportion to the HCO_3^- concentration do the deviations become too great, because in this case the CO_3^- ions, resulting from HCO_3 by further dissociation, can no longer be neglected. Tillmans assigns 1:40 as the limiting ratio.

Just as the CO_2^- content alone fails to give a picture of the aggressivity of the water, so, too, are we unable to form an opinion thereon on the basis of pH. Just as to each concentration of $Ca(HCO_3)_2$ which the water may have there belongs a certain concentration of free CO_2 which is necessary to retain this $CaCO_3$ in solution, which CO_2 will exhibit no aggressive properties with respect to chalk, cement, etc., so, too, to every $Ca(HCO_3)_2$ concentration belongs a certain pH. Only when this concentration of H-ion is exceeded does the water exhibit aggressive characteristics with respect to the substances mentioned above. In such water the material of the mains is not coated with a protective layer of $CaCO_3$ and thus phenomena of corrosion may arise, of which, from the point of view of sanitary significance, the attacking of lead is the most dangerous.

Tillmans has calculated the "appropriate" pH for water of different HCO_3^- concentration and has assembled the data in a table.

In table 5 are given for a number of samples of water, first the three figures found by direct determination for HCO_3^- content, pH, and free CO_2. Further, the last column but one gives the difference between the pH found and that appropriate to the carbonate hardness; and finally in the last column is given the concentration of aggressive CO_2 calculated with the help of Tillmans' table. These samples were collected on different dates and are therefore not suited for mutual comparison, such for example as "prefiltered" with "filtered," etc. They are given merely as arbitrarily chosen examples to bring out the correspondence between theory and practice.

TABLE 5

SOURCE OF SAMPLE	BICARBONATE	$\frac{(H)}{10^{-7}}$	CO_2	APPROPRIATE CO_2	APPROPRIATE $\frac{(H)}{10^{-7}}$	DIFFERENCE IN $\frac{(H)}{10^{-7}}$	AGGRESSIVE CO_2
Zwarteveld no. 5	303.6	0.45	49.0	96.7	0.96	−0.51	−47.7
Westerveld no. 6	162.8	0.32	17.4	15.2	0.23	0.09	3.4
Westerkan no. 7	136.4	0.18	9.0	7.0	0.15	0.03	0.8
v. Stirumkanaal source 60	224.4	0.43	31.8	37.5	0.51	−0.08	−5.7
v. Stirumkanaal source 70	162.8	0.33	17.9	12.2	0.23	0.10	3.7
Westerkan source 20	246.4	0.24	19.3	28.1	0.64	−0.40	−32.1
Leiduin Ruw	202.4	0.13	8.8	26.1	0.38	−0.25	−17.3
Leiduin Voorfiltr	200.2	0.23	14.9	25.0	0.37	−0.14	−10.1
Leiduin Nafiltr	200.2	0.10	6.6	25.0	0.37	−0.27	−18.5
Vechtw. Bezonken	136.4	0.14	6.5	7.0	0.15	−0.01	−0.5
Vechtw. Reinw	136.4	0.18	7.5	7.0	0.15	0.03	0.4
Bronwater	70.4	0.26	5.8	1.4	0.06	0.20	4.1
Diepb. Z. 4900, p. 3	334.4	0.31	35.2	127.0	1.14	−0.83	−91.8

From the concentration of HCO_3^- and of free CO_2 can, as we have seen, the pH be calculated. While of course, vice versa, we can also, from the first and second determination, calculate the free CO_2. In this way we have a control over these figures. The calculation of the CO_2 is very advantageous, for example, when we have an iron-containing water, the CO_2 content of which is difficultly determinable by direct titration, or impossible to determine entirely, while we, by taking a few precautions in order to exclude as far as possible the oxygen of the air, and working rapidly, preferably on the spot where the sample is taken, can determine very closely the HCO_3^- content and the pH, and from these can calculate approximately the CO_2, so that we have results of value for practical purposes, as a control by determination of the total CO_2 content will show. Apart from interference by iron, absolutely exact results are not to be expected, inasmuch as Tillmans assumes a complete dissociation of Ca $(HCO_3)_2$. This may very well be the case for water which has but little $Ca(HCO_3)_2$, such for example as the Amsterdam Bron water; for the very hard dune water we should in this way fall into error, and should find a higher value for the CO_2 calculated after Tillmans than that obtained by direct titration. As, however, the CO_2 concentration in the samples examined is small, and it is difficult to titrate closely such small concentration, no striking figures were obtained in this respect.

TABLE 6

SAMPLE	pH FOUND	pH CALCULATED	$\frac{(H)}{10^{-7}}$ FOUND	$\frac{(H)}{10^{-7}}$ CALCULATED	BICARBONATE	FREE CO_2 FOUND	FREE CO_2 CALCULATED	$\frac{CO_2 \text{ FOUND}}{CO_2 \text{ CALCULATED}}$
v. Stirumk. br. 60	7.37	7.37	0.43	0.43	224.4	31.8	32.2	1.01
Leiduin Ruw	7.88	7.90	0.13	0.13	202.4	8.8	8.8	1.00
Leiduin Voorf	7.80	7.80	0.16	0.16	200.2	10.5	10.7	1.01
Leiduin Reinw	8.00	8.05	0.10	0.09	195.8	6.1	6.5	1.07
Vechtw. bezonken	8.20	8.15	0.06	0.07	162.8	3.7	3.3	0.89
Vechtw. Reinw	7.95	8.00	0.11	0.10	140.8	4.6	5.2	1.13
Bronwater	7.58	7.60	0.26	0.25	70.4	5.8	6.1	1.05
Leiduin filt. 3	7.70	7.73	0.20	0.19	202.4	12.7	13.5	1.06
Diepb. W. 510, p. 5	7.70	7.62	0.20	0.24	228.8	17.6	15.3	0.87
Diepb. Z. 4900, p. 6	7.58	7.53	0.26	0.27	215.6	19.1	18.7	0.98

That we can nevertheless very well adopt Tillmans simplified formula in practice is seen from table 6 for water of various composition from the Amsterdam water supply. In the last column is given the ratio of the CO_2 found to the calculated concentration.

We can thus, as appears from the above consideration, deduce the concentration of aggressive CO_2 from the pH and the carbonate hardness, two determinations, both of which we can effect on the spot, which for practical purposes, is of the very greatest importance. Moreover it is not necessary that we should first calculate the free CO_2 from these data, in order to determine the concentration of aggressive CO_2 either by help of Tillmans' table or Auerbach's curve: but we can very closely predict this last by subtracting from the pH found, the pH appropriate to the HCO_3^- concentration found, and dividing the result by 0.03. This method of calculation is, however, not exact for water which has less than 100 mgm. bicarbonate CO_2 per liter; while its accuracy further decreases according as the content of aggressive CO_2 increases. With a content of aggressive CO_2 of 25 mgm. per liter, the error amounts to about 2 mgm. Thus even in this case results of value for practical purposes are obtained.

In the same way as Tillmans has adapted the law of mass action for the calculation of pH in CO_2-rich water, we can do this for CO_2-free water, such as was found this year in the sedimentation basins and the filters of the Weesperkarspel Pumping Station.

We have in this case to do with a mixture of carbonate and bicarbonate, the concentration of which can be obtained by titration with HCl, using respectively methyl-orange and phenolphthalein as indicators. From the formula of the mass-action-law, since in this case

$$HCO_3^- \rightleftarrows H^+ + CO_3^{--}$$

it follows that:

$$\frac{(H^+) \,.\, (CO_3^{--})}{(HCO_3^-)} = K_2$$

or

$$(H^+) = K_2 \times \frac{(HCO_3^-)}{(CO_3^{--})}$$

where

$$K_2 = 6 \times 10^{-11}$$

When we have to deal with a CO_3^{--} concentration which is very small in comparison with the HCO_3^- concentration, we cannot neglect the CO_3^{--} ions derived from the bicarbonate ions in accordance with the equation:

$$2\ HCO_3^- \rightleftarrows H_2CO_3 + CO_2$$

and we can, in a similar way to that in which Tillmans has done it for carbonic acid containing water, develop an accurate formula for the calculation of pH.

We find then:

$$(H^+) = \sqrt{\frac{K_1K_2a}{a + 2b} + \left(\frac{bk_1}{2a + 4b}\right)^2} - \frac{bk_1}{2a + 4b}$$

Where a denotes bicarbonate CO_2 concentration and b the free CO_2 concentration, both expressed in milligram per liter.

Auerbach and Pick have followed this method in order, from the pH, the (HCO_3^-) and the (CO_3^{--}) concentration to determine the value of K_2.

If the (CO_3^{--}) is not too small in proportion to the (HCO_3^-), we can then make use of the simple formula:

$$(H^+) = 6 \times 10^{-11} \frac{\text{bicarbonate } CO_2}{\text{carbonate } CO_2}$$

The author has examined more closely how far it is necessary to use for the Merwede Canal water the very complicated accurate formula, and has to this end calculated the pH for various concentrations of CO_3^{--} according to the two formulae. At the same time he gives in table 7 the (OH^-) which is more rational for these alkaline waters. For this the value $K_w = 0.74 \times 10^{-14}$ (18°C.) has been assumed.

TABLE 7

BICARBONATE	CARBONATE	H-ION CONCENTRATION $\times \frac{1}{10^{-7}}$		OH-ION CONCENTRATION $\times \frac{1}{10^{-7}}$		H EXPONENT	
		Simple formula	Accurate formula	Simple formula	Accurate formula	Simple formula	Accurate formula
140	8	0.0105	0.0100	71	74	8.98	9.00
140	6	0.0140	0.0127	53	58	8.85	8.90
140	4	0.0210	0.0174	35	42	8.68	8.76
140	2	0.0420	0.0259	18	28	8.38	8.57

From this it is apparent that for water which contains such low concentrations of CO_3^{--} as were here found for the Merwede Canal (the greatest concentration of CO_3^{--} amounted to 4.8 mgm. per liter of carbonate—CO_2) we can no longer employ the simple formula.

The titration of such small concentrations of CO_3^{--} moreover occasions so much difficulty, that it is actually desirable to reverse the procedure and calculate the CO_3^{--} concentration from the pH and the HCO_3 concentration.

Three more examples from actual working, relating to settled Merwede Canal water, are given in table 8.

That the pH value found does not always give a good agreement with the calculated has its reason chiefly in this, that it is difficult accurately to determine such small CO_3^{--} concentrations as are here in question. Moreover, the author has, as Tillmans also did, assumed in his calculations that the Ca^{++} salts in the water are completely dissociated, which is not actually the case. In this way, too, an error is introduced, even if it be of little practical significance.

TABLE 8

DATE	BICARBONATE CO_2 IN MILLIGRAMS PER LITER	CARBONATE CO_2 IN MILLIGRAMS PER LITER	pH FOUND	pH CALCULATED
March 30	141.2	4.4	8.60	8.80
April 6	135.5	4.8	8.70	8.79
April 13	140.0	2.6	8.48	8.61

Summarizing the conclusions to which the above-described experiments have led, we can thus say:

1. From Guldberg and Waage's Law of Mass Action the relations between the pH the concentration of the bicarbonate CO_2 and the concentration of free CO_2 may be calculated.

2. This relation is, as Tillmans has pointed out, very simply to be represented by formula:

$$h^{\cdot} = \frac{3 \times \text{free } CO_2}{\text{bicarbonate } CO_2}$$

where $h^{\cdot}$ represents the concentration of H^+ expressed in ten thousandths milligram per liter, while the free CO_2 and bicarbonate CO_2 are expressed in milligrams per liter.

This formula is only approximate: but it is for the majority of cases sufficiently accurate for practical purposes.

3. Whenever we have determined two of the above mentioned values, we can thus always calculate the third.

This has its application in the water supply business when for instance the direct CO_2 determination by titration presents difficulties, as is the case in presence of iron salts.

When all determinations can be made then the formula gives us a convenient method to control the values found.

4. If the water has no free CO_2, which case as we have seen may actually occur in practice, we can again adopt the law of mass-action which in this case leads to the formula:

$$(H^+) = \sqrt{\frac{K_1K_2a}{a + 2b} + \frac{(bk_1)^2}{(2a + 4b)^2}} - \frac{bk_1}{2a + 4b}$$

where a denotes the bicarbonate CO_2 and b the carbonate CO_2, both expressed as milligram per liter.

If the CO^{3--} concentration is not too small in proportion to the HCO_3^- concentration we can use the simple formula:

$$(H^+) = 6 \times 10^{-11} \times \frac{\text{bicarbonate } CO_2}{\text{carbonate } CO_2}$$

5. In this connection, the indicator method for pH determination can give good service, because we can carry it out in the field, which is in most cases desirable and in some cases imperative.

6. When we have determined the pH and the carbonate—hardness of water, we can then in a very simple way approximate to the concentration of aggressive CO_2 by dividing by 0.03 the difference between the "pH" found and that which corresponds to the hardness found, both expressed in ten thousandths milligram per liter. We obtain thus results sufficiently accurate for practice provided the bicarbonate CO_2 concentration is not less than 100 mgm. per liter.